Aqueous Methods for the Cleaning of Painted Surfaces

Day 2: Thickeners, Spreadable Gels, Hydrogels; Clearance and Residues

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Baltic-American Freedom Foundation

Art Academy of Latvia

VALSTS KULTŪRKAPITĀLA FONDS

LATVIJAS RESTAURATORU BIEDRĪBA

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
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1

Session Outline

- **Some loose definitions**
  - Thickeners, aqueous gels, hydrogels
- **Why gels? Useful properties for cleaning**
  - Practical considerations
  - Gel rheology
- **Gel materials in aqueous cleaning applications**
  - Cellulose ethers, Pemulen TR-2, xanthan gum, sclerotium gum
- **Hydrogels**
  - Agarose, Nanorestore gels, xanthan/locust bean gum gels, curdlan

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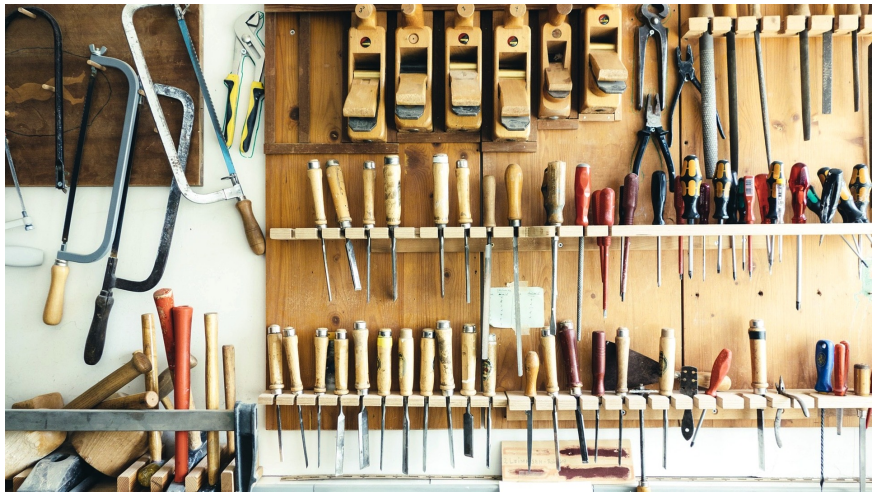
2



3

Some Loose Definitions

Thickener / Thickening Agent

A hydrophilic, relatively high-molecular-weight material added to a solution to **increase viscosity** *with little influence on the structure or fluid dynamics of the solution*

Aqueous Gel

A solution with a concentration of thickening agent:

- having a **semi-solid**, weakly cohesive structure
- having **varied response to applied shear**

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4

Some Loose Definitions

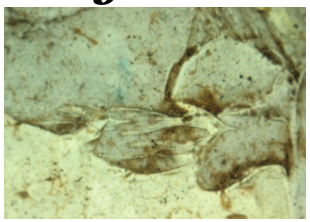
Hydrogel

A **hydrophilic**, three-dimensional network of **entangled and/or cross-linked** polymeric material containing **>~90% water**.

Despite its high water content, the hydrogel is not soluble in water!

5

Why Gels?



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Why Gels?

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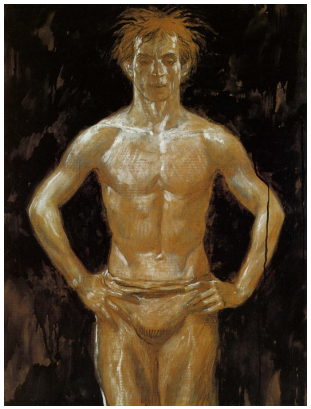
Why Gels?



Jamie Wyeth, ***Nureyev***, 1977

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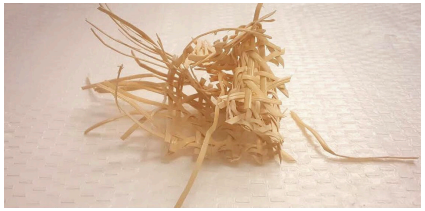
8

Why Gels?



9

Why Gels?

Josh Sarantitis
Legacy
Philadelphia, Pennsylvania, USA
Completed 2006

10

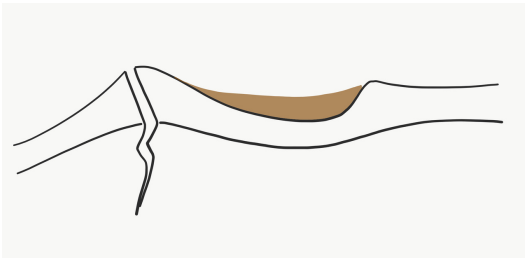
Why Gels? Practical Considerations

- Handling Properties: Control!
- Health & Safety
- Economic Considerations
- Synergy with Other Aqueous Solution Parameters!

11

Useful Properties to Exploit

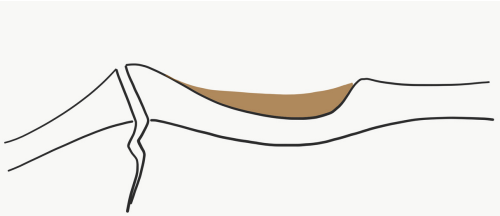
- Increased viscosity
- Shear thinning
- Gel cohesion
- Elasticity/Rigidity
- Water retention



12

Useful Properties to Exploit

- Solvent stabilization/ Emulsification
- Thermo-reversibility/ Heat stability



13

KEY CONCEPTS

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14

Factors Determining Gel Properties & Rheology

- **Thickener/gel molecular weight & concentration**

- **Polymer/oligomer structure**
  - Straight vs. branched
  - Regularity/homogeneity of repeat units
  - Degree of substitution: frequency of side chains
  - Hydrophilic & hydrophobic substructures
  - If hydrophilic: Ionic? Hydrogen bonding?

15

Factors Determining Gel Properties & Rheology

- **Solution parameters ("solvent quality")**
  - pH – gel stability; ionization state of acid groups
  - Ionic environment (conductivity, e.g.)
  - Presence of divalent metal ions (Ca^{2+}, e.g.) – ionic crosslinking
  - Co-solvents' concentration and solubility parameters

- **Processing**
  - Physical mixing
  - Crosslinking (chemical gels)
  - ***Temperature processing***

16

Gel Polymers

- Natural polymers
  - Proteins
  - **Polysaccharides**

  Simple preparation
- Synthetic polymers
  - In theory: great variety of options
  - In practice: additional processing requirements
  - **Increased possibilities for crosslinking** (chemical gels)

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17

Factors Determining Gel Properties & Rheology

Intentional polymer selection, concentration, appropriate thermal processing, solution formulation will result in gels that:

- ***are brittle, tough, elastic, stiff, loose, cohesive, fluid***
- ***control delivery of aqueous chemistry***
- ***provide beneficial working properties for the conservator***

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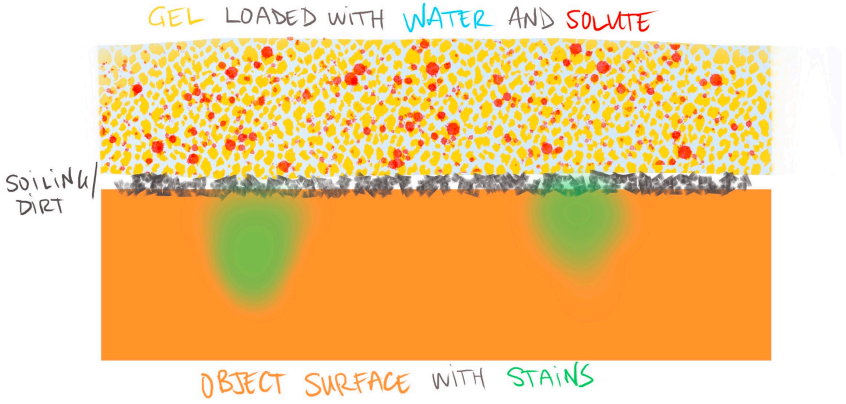
18

Mass Transfer in Gel Cleaning



19

Mass Transfer: Practicalities

- **Predicting mass transfer can be difficult:**
  - Heterogeneous gel pore/mesh size
  - Gel surfaces often have small flaws
  - Surface contact can be incomplete
  - Unpredictable interactions between solutes & gel matrix
  - Unpredictable influence of object porosity, condition, treatment history etc. etc. etc.

20

Mass Transfer: Practicalities

- **Questions to ask:**
  - *Are we able to control the delivery of moisture?*
  - *Is the solution achieving the desired result?*
  - *Is the time scale appropriate?*
  - *Are solubilized/affected materials sorbed into/onto the gel, or do they remain at the surface of the object?*
  - *Once cleaning is complete, are there signs of residues from the gel matrix and/or the delivered solution?*

21

Useful Equipment

- **Scale**
  - Ideally: accuracy better than 0.05g (kitchen scales < USD 20.00)
- **Mixers**
  - Magnetic stir plates (some compact units < USD 40.00)
  - Battery-powered milk frothers/mixers (USD 6.00–20.00)
  - Stir rods, spatulas

22

Useful Equipment

- Hot plate
  - For water baths (search for home brewery equipment)
- Immersion circulator
  - For precision temperature control (some models USD 60.00)
- Microwave

23

23

Measuring pH of Gels

- **Use enclosed, all-in-one electrodes**
- **“Swiss spear” type meant for soft foods; flat surface probes**
- **pH indicator papers or test strips**

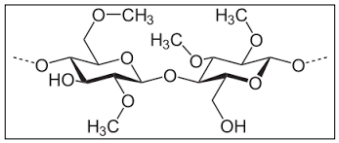
24

24

SELECTED SPREADABLE GEL MATERIALS

25

Cellulose Ethers



Broad range of substituted celluloses

- Methylcellulose, HPMC, HEC, CMC…
- Can be nonionic or anionic (Sodium CMC, e.g.)
- Grades vary in degree of substitution, molecular weight

Practical Considerations

- **Inexpensive**
- Soluble in **cold water**
- Prone to agglomeration, foaming during formulation
- **Concentration in solution will depend on selected product and desired properties!**

26

Cellulose Ethers

Very good general-purpose thickeners:

- **Compatible with pH, conductivities common in conservation cleaning**
- **Compatible with redox reagents**
- **Compatible with enzymes, resin/bile soaps, surfactants**
- **Some solvent stabilization, depending on substitution**
- **Shear-thinning (pseudoplastic) behavior**

Other applications: hydration of adhesive residues; adhesive/consolidant

27

Cellulose Ethers

Name	Type*	Usage Ratio	Solubility	Viscosity @2%	Gelling Temp	Gel Strength
SGA7C	MC	0.1-3%	Cold	700cp (med)	100-114F (38-44C)	Very Firm
A15C	MC	0.1-3%	Cold	1500cp (med)	100-114F (38-44C)	Firm
A4C	HPMC	0.1-3%	Cold	400cp (low)	100-114F (38-44C)	Firm
E4M	HPMC	0.1-3%	Cold	4000cp (high)	136-147F (58-64C)	Semi-Firm
F50	HPMC	0.1-3%	Cold	50cp (very low)	143-154F (62-68C)	Semi-Firm
K100M	HPMC	0.1-3%	Cold	100,000cp (very high)	158-194F (70-904C)	Soft
LV	MC	0.5-0.75%	Cold	450cl (low)	118-132F (47-55C)	Soft
HV	MC	0.5-0.75%	Cold	4500cp (high)	132-148F (55-64C)	Soft

*MC – Methycellulose. HPMC - Hydroxypropylmethylcellulose

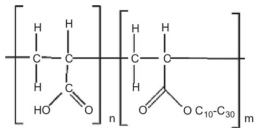
https://blog.modernistpantry.com

Gel Temperature

- Generally unimportant for cleaning applications
- Forms a thermo-reversible gel in narrow ranges

28

Pemulen TR-2



Copolymer: poly(acrylic acid)/C10-C30 alkyl acrylate

- C10-C30 alkyl acrylate present in blocks
- White powder
- Fairly easy formulation

Practical Considerations

- **Inexpensive (USD 8.00/100g)**
- No temperature processing necessary
- **Must be neutralized** to form a gel
- Typical concentrations: **1–1.5%**
- **Able to form stable emulsions with non-water-miscible solvents**

29

Pemulen TR-2: Neutralization

Neutralization/deprotonation of acrylic acids

- **Must add a base** to the solution
- Deprotonation provides charge repulsion, allowing for hydration and **unfolding of the polymer**
- Common options: sodium hydroxide, triethanolamine

Some thoughts about triethanolamine:

- **Imparts some solvent parameters to the solution**
  - HSP: dd 17.3, dp 22.4, dh 23.3
- **Can buffer the solution (7.3–8.3)**
- **Can be a good complexing agent for Al^{3+}!**

30

Pemulen TR-2: Formulations

Stock solution for testing:

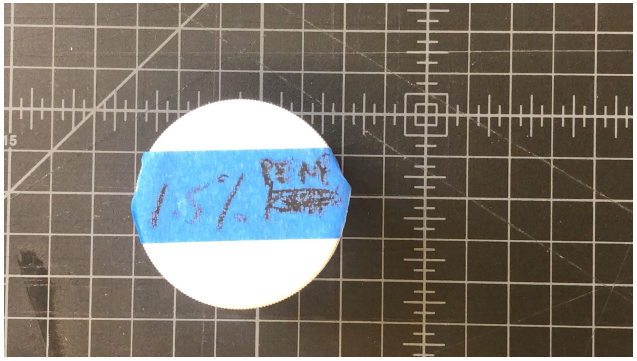
- 2% Pemulen TR-2, distilled/deionized water, base
- With clean glassware and tools, rare microbial growth
- Can add a preservative (phenoxyethanol, Germaben)
  - ***Omit preservative in final cleaning formulation!***

Using the stock solution:

- Measure out a volume of stock Pemulen TR-2
- Add equal volume concentrated aqueous solution (2x buffer, 2x chelator, **1x conductivity**)
- Most stable between pH 6–9

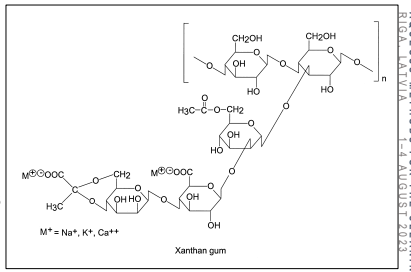
31

Pemulen TR-2: Formulations



32

Xanthan Gum



Xanthan gum

Bacterial branched ionic gum

- Cellulose backbone
- Anionic trisaccharide side chains

Practical Considerations

- **Inexpensive (USD 6.80/100g)**
- No temperature processing necessary
- **Readily hydrates in cold water**
- Typical concentrations: **0.75–1.5%**
- **Very viscous solutions**
- Exceptional **shear thinning**

33

Xanthan Gum: Formulations

Stock solution for testing:

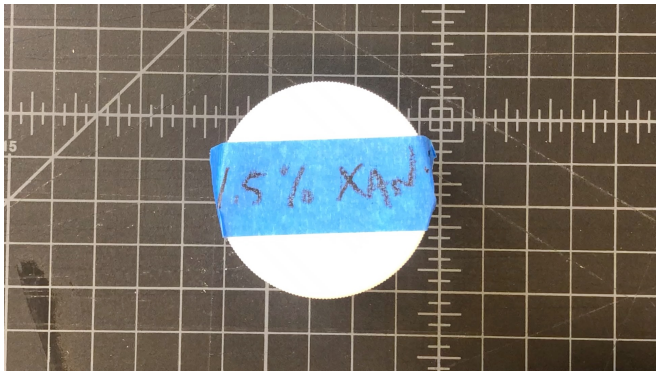
- 2% xanthan, distilled/deionized water
- Even with clean glassware and tools, ready microbial growth
- Add a preservative (phenoxyethanol, Germaben)
  - ***Omit preservative in final cleaning formulation!***

Using the stock solution:

- Measure out a volume of stock xanthan solution
- Add equal volume concentrated aqueous solution (2x buffer, 2x chelator, 2x conductivity)
- Stable between pH 2–12

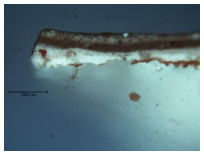
34

Xanthan Gum: Formulations



35

DTPA Case Study: Washington Portrait, c. 1810.



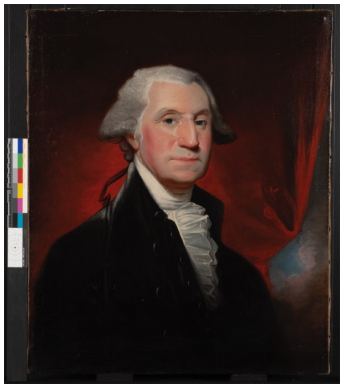
36

DTPA Case Study: Washington Portrait, c. 1810.

- 0.5% DTPA, buffered to pH 5.5, 1.5% **xanthan gum**
- Hydrophobic solvent applied to inhibit gel ingress
- Agitation with a brush under magnification
- Cleared with pH 5.5 'pH adjusted water' from MCP

37

DTPA Case Study: Washington Portrait, c. 1810.

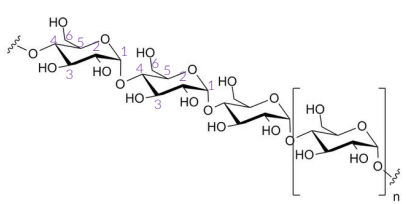


38

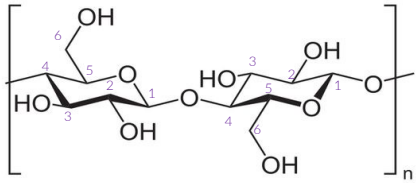
HYDROGEL CONCEPTS

39

Polysaccharide Structures



Amylose: (1→4)-α-D-glucose



Cellulose: (1→4)-β-D-glucose

40

Polysaccharide Chain Structures

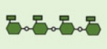
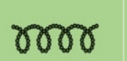
	Cellulose	Starch		Glycogen
		Amylose	Amylopectin	
Source	Plant	Plant	Plant	Animal
Monose	β-glucose	α-glucose	α-glucose	α-glucose
Glycosidic bonds	1-4	1-4	1-4 and 1-6	1-4 and 1-6
Diagram				
Shape				

Fig. 1.1 Examples of molecular chain structure of polysaccharides

41

Polysaccharide Selection

- **Rigid, brittle gels:**
  - More homogenous (homopolymers)
  - More crystalline in behavior (linear, rod-like structures)
  - Fewer side chains, less branching
  - Increased junction density (crosslinking, chain entanglement)
- **Flexible, elastic gels**
  - Heteropolymers and branched polymers
  - Polymer networks capable of significant swelling
  - High density of strong and weak chain-chain interactions

42

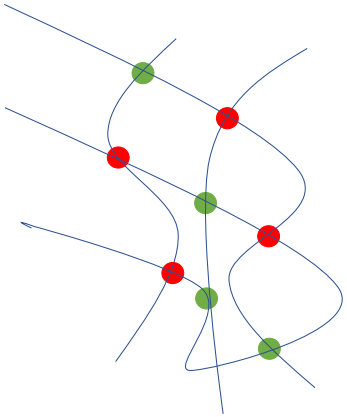
Effect of Processing

By **adding enough energy** to the system, we allow polymer chains to fully hydrate and exist as **random coils in solution**.

Random coils then self-arrange to concentrate hydrophobic interactions (CH_2 backbone) and hydrophilic interactions (hydrogen bonding, coordinated water, ions) to form a **somewhat regular structure**

43

Factors Determining Gel Physical Properties

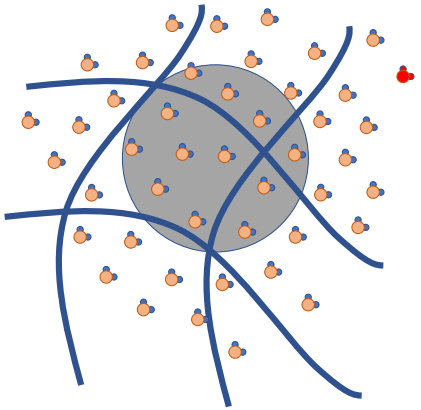


Polymer concentration,
cross-link/entanglement density,
and solvent quality

determines mesh size or “pore size”

44

Diffusion in Hydrogels



- **Solutes will diffuse through hydrogels if:**
  - It would normally diffuse freely in a solution of the same composition
  - The solute is smaller than the mesh/pore size of the hydrogel
- **Diffusion will be inhibited if:**
  - The solute encounters an energetically favorable location
  - The average mesh size ≤ solute size

45

Capillary Action in Hydrogels

- **In simplistic terms:**
  - Capillary action is driven by **surface forces** between the gel material and the liquid phase
  - Capillary action is **spontaneous** and occurs without the application of external pressure
  - A simple model of capillary action in hydrogels: a bundle of tubes with a uniform radius

In a hydrophilic, porous medium, it is expected that capillary forces will imbibe water into the structure.

46

Syneresis

- With applied stress, and relaxation of stress, the microstructure of the gel can be altered:
  - Helical structures can tighten
  - Physical bonds can break and reform
  - The gel structure can become more dense
- and water can be expelled spontaneously: syneresis!
- Syneresis can be caused by slight temperature changes, gel "maturation", introduction of differing solvent quality

47

General Trends: Rheology and Moisture Retention

With decreasing pore size:
- ***Decreased rates of diffusion***
- ***Increased capillary action***

Increased polymer concentration and junction density will increase moisture retention

With increasing brittleness:
- ***Increased syneresis***

Flexible, elastic gels will exhibit decreased syneresis

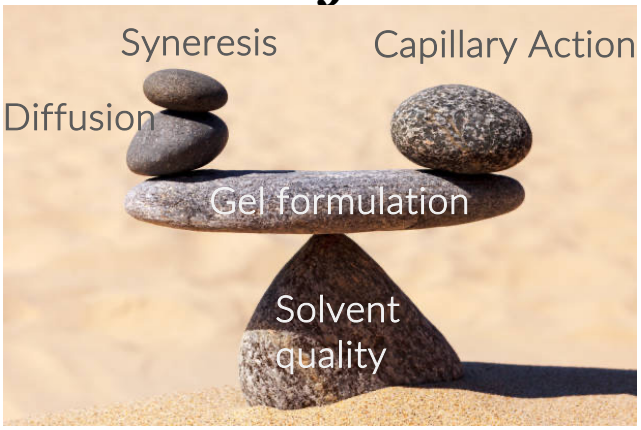
48

General Concepts: Hydrogels

- Think of hydrogels as a "vessel" for delivering water/moisture
- Lower polymer concentration: more open structure; vessel empties faster
- Better surface contact: more efficient diffusion and capillary action
- Smaller mesh/pore size: increased capillary action, but slower delivery. *Testing will help you to find the balance!*

49

Moisture Delivery and Retention



50

HYDROGEL FORMULATION FOR CONSERVATORS

51

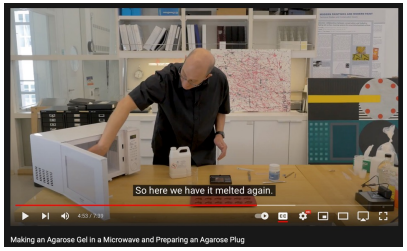
Water Bath Method

- Set bath temperature above the hydration/melting temperature
- Disperse polymer in distilled water (or other solution) in a well-sealed container
- Submerge container in bath; remove periodically to mix contents
- Allow the contents to reach the bath temperature; remove from bath
- As solution cools, but before gelation, pour into mold

52

Microwave Method

- Disperse polymer in distilled water in a **microwave-safe container. Cover loosely!**
- Microwave on **half power** for 20-30s, 3-5x total
- Remove from microwave and swirl after each heating
- **Avoid allowing the solution to boil over!**
- As solution cools, but before gelation, pour into mold



https://www.youtube.com/watch?v=V490KuFsU4k

53

Useful Equipment - Molds

- Silicone molds – food prep, baking, candy making
- Glass containers – Petri dishes, watchglasses, ashtrays
- Pyrex dishes
- Mylar/ Melinex trays

54

Useful Equipment - Molds

55

Incorporating Aqueous Cleaning Solutions into Hydrogels

<u>Option 1: Loading prepared solutions into prepared gels</u>

- Prepare the hydrogel and aqueous solution separately
- Place the gel sheet/block in the solution for 12-24 hours
- Blot the gel so that there is no liquid solution at the surface
- Place the gel sheet/block on the target surface
- Repeat applications may be necessary

This is the most reliable method for ensuring that gel properties are not compromised.

56

Incorporating Aqueous Cleaning Solutions into Hydrogels

Option 2: Prepare the gel with aqueous cleaning agents

- Include buffer, ionic material, chelating agents into the initial formulation
- If preparing a gel that forms during cooling, add temperature-sensitive ingredients (surfactants, enzymes, e.g.) once the solution has reached a safe temperature, before reaching the gelation temperature.
- Blot gel to remove surface liquid solution before use.

Most chelating agents, salts, and buffers used in conservation can be heated to the necessary temperatures

57

AGAR & AGAROSE

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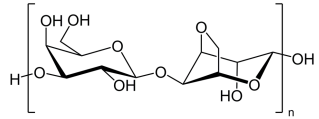
58

Agar - Industrial Production

- **Agar** is a biopolymer contained within cell walls of red algae
  - Major component: **agarose**



  - Fraction inhibiting gelling: **agaropectin(s),** a complex mixture of carbohydrates and sulfates thereof

- Cold waters → thicker cell walls (**more to extract**)

Geographical location, environmental factors contribute to product quality

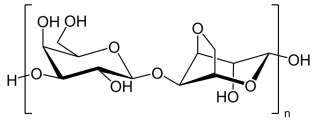
59

Usable Agar Products

- **Food-grade agar - *~10-30 USD/100g***
- **Technical agars (bacteriological) - *~30 USD/100g***

60

Agarose



Purified biological extract from red algae species

- Repeating disaccharide, agarobiose

Practical Considerations

- **Very expensive (USD 104.00/100g)** for pure material
- Requires heating **beyond melting temperature**
- Forms a **rigid, brittle gel** upon cooling below gelation temp.
- Thermo-reversible
- **Gel pore structure depends on solution concentration**

61

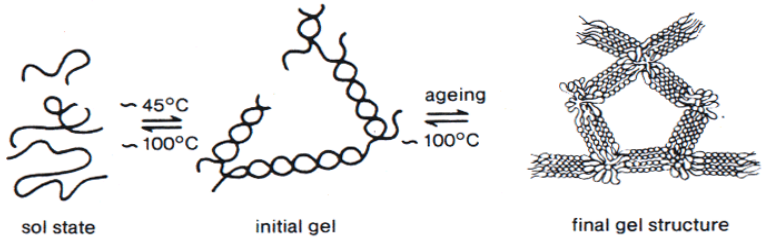
Agarose

One method for producing a 5% agarose gel:

- Mix 5% w/v agarose in distilled water
- Microwave on half power, 20s, three times
- Remove from microwave and swirl in between heatings
- Do not allow the agarose to boil over
- Remove from microwave. Stir as it begins to cool.
- As the solution cools, but before gelation, can add:
  - Preservative, enzymes, buffers, chelators…

62

Agarose Structure

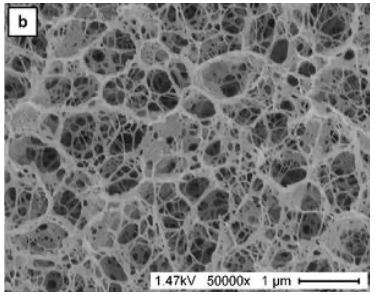


Upon cooling, gel remains <u>water insoluble</u>, but hydrophilic.

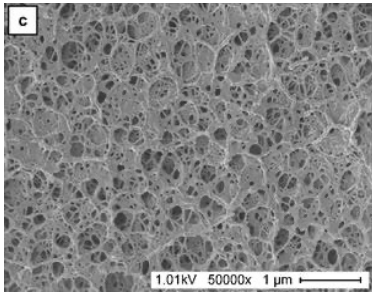
Can load aqueous solutions, microemulsions, some polar solvents for surface delivery.

63

Agarose Structure



2% Agarose



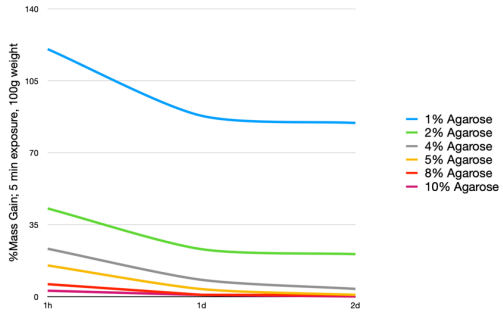
6% Agarose

Porous structure determines retention & rate of diffusion.
*Also exhibits **syneresis – a self-expression of surface moisture***

64

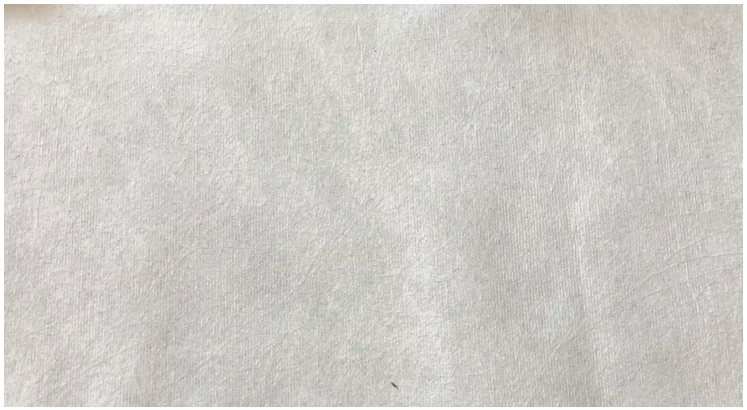
Agarose Moisture Delivery/Retention

- Greater gel concentration :: greater retention
- 'Fresh' gels :: lesser retention



65

Agar & Agarose Properties



66

Agar or Agarose? Which Type?

- **What is the goal of the treatment step?**
  - Simple hydration/humidification: **Agar ($)**
  - Increased gel flexibility: **Agar**
  - Large surface areas: **Agar ($)**
  - Controlled hydration/humidification: **Agarose**
  - Controlled delivery of aqueous cleaning solutions: **Agarose**
  - Aqueous cleaning on water-sensitive surfaces: **Agarose**
  - Controlled delivery of temperature-sensitive reagents: **Low-gelation-temperature agarose (Very expensive!)**

Preferred agarose: Agarose LE (low electroendosmosis).

67

AGAR & AGAROSE IN CONSERVATION: *Applications*

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
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68

Agar & Agarose – Cold Methods

- **Use of cast agarose:**
  - Surface testing
  - Controlled moisture delivery
  - Stain reduction/poulticing
  - Surface cleaning

69

Estimating Surface pH and Conductivity

Erica Rota, Claudio Bozzi, Paolo Cremonesi & Anna Lucchini (2021) Study of the Best Methodology for Measuring Surface pH of Linen Canvas, *Studies in Conservation*, 66:6, 313-320, DOI: 10.1080/00393630.2020.1838711

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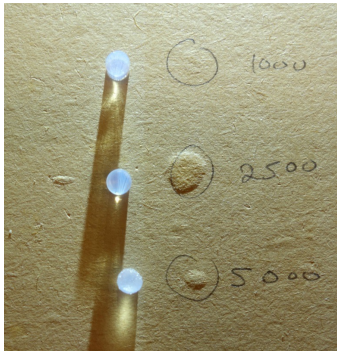
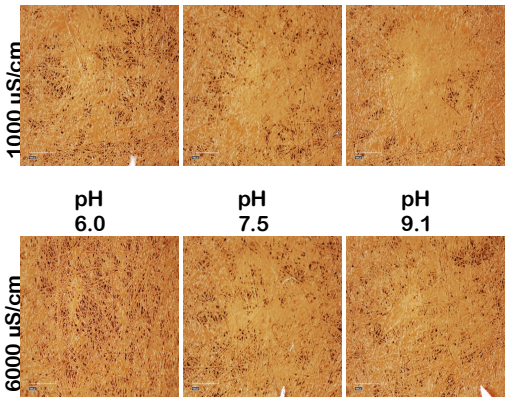
70

Testing Surface Swelling





71

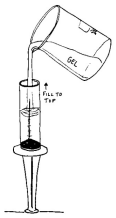
Large-Scale Stain Reduction

Figure 4 Diagram of beveled agarose gel with weight.

Samantha Skelton, Corina Rogge & Zahira Véliz Bomford (2016) Testing the limits: The theoretical development and practical reality of a large-scale agarose gel treatment for a discolored Morris Louis, *Studies in Conservation*, 61:sup2, 214-218, DOI: 10.1080/00393630.2016.1181865

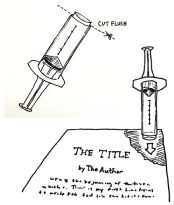
72

"Stain Stick"



4. CAST THE GEL
While the gel is still hot and liquid, pour it carefully into the cut open end of the syringe. Standing the syringe on the end of the plunger is usually stable – if it is not, have a partner hold it for you. Pour excess gel into other prepared syringes or into a flat, heat-proof container for use as a cast gel. The syringes take longer to set than cast gels because they retain heat longer in their cylindrical shape! Leave the gel for at least thirty minutes to ensure it is fully set. The agarose will appear slightly hazy and blue when set.

5. USE THE GEL
Push the plunger down slightly to expose the gel. With a clean blade, cut the gel flush with the plastic syringe to trim off the meniscus of the gel. The "Stain Stick" is now ready to use! Lightly pounce on your object where necessary; longer dwell time or more pressure will release more water. Try cutting the tip of the gel into a chisel or point for detailed work! Avoid vigorous rubbing across the object's surface, which can cause crumbling of the gel and abrasion of the object's surface. As the end of the gel becomes stained with imbibed discoloration products, trim it off with a clean blade. Store the gel in a plastic bag and in the refrigerator for up to two or three weeks.



SYRINGE-CAST AGAROSE HANDOUT, M. BROCKMAN, ED. 2020 | 2

Image: Madison Brockman, AIC BPG

73

73

Agarose – Grated Crumbs

Cremonisi (2016)

Brittle agarose gel can be grated or pushed through a screen to create agarose crumbs

Crumbs can be loaded with an aqueous solution and worked across a surface like eraser crumbs

74

74

Fragmented Gels

75

Warm Application/In-situ Casting

Concerns:

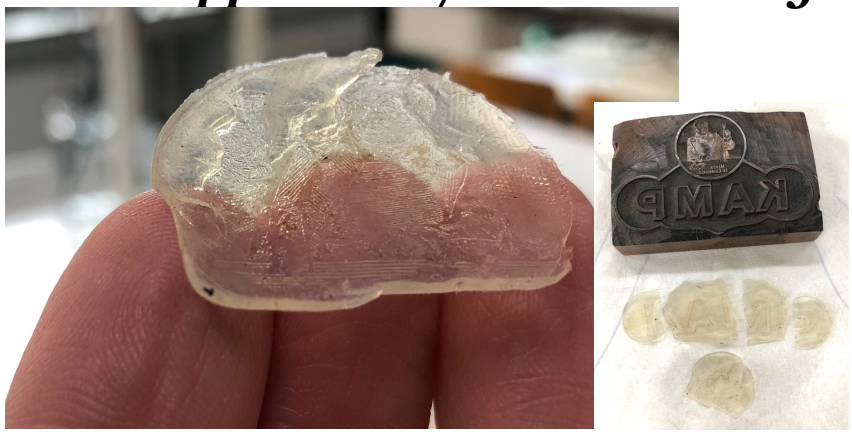
- **Temperature stability of original surface**
- **Ingress of fluid solution into cracks and pores**
- **Personal safety: Hot gel and exposed skin are a bad mix!**

But consider:

- If the gel temperature is sufficiently low, you can wait to apply the warm solution to the surface just before gelation
- If the gel concentration is high, you can expect faster gelation, limiting ingress
- Temporary hydrophobization may protect cracks and pores

76

Warm Application/In-situ Casting



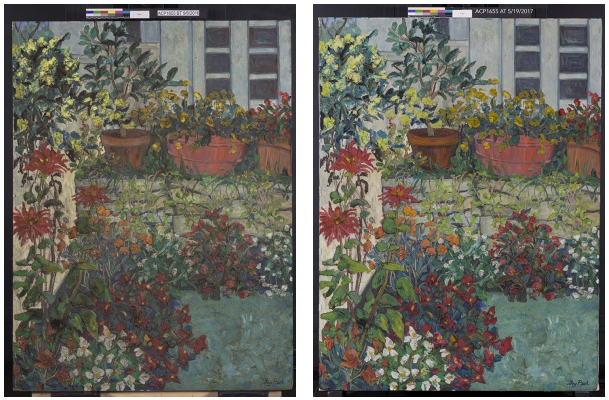
77

Agarose – Warm Brush/ Poured Application

Diana Hartman, Laura Eva Hartman & Caroline Hoover (2019) Experimenting with Agarose: New Methods for Cleaning Sensitive Modern and Contemporary Surfaces, AIC Paintings Specialty Group Postprints 32, 157-172.

78

Agarose – Warm Brush/ Poured Application



79

Agar – Sprayed Application

Ambra Giordano & Paolo Cremonesi (2021) New Methods of Applying Rigid Agar Gels: From Tiny to Large-scale Surface Areas, Studies in Conservation, 66:8, 437-448, DOI: 10.1080/00393630.2020.1848272

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
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80

ADDITIONAL TARGET GEL PROPERTIES

81

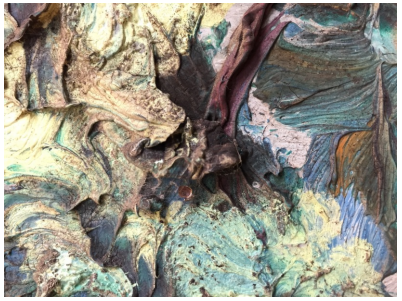
Target Property: Flexibility

Rigid gels on rough surfaces:

- Uneven moisture delivery
- Lesser capillary action

Flexible gels:

- Improved surface conformation
- More consistent cleaning on rough surfaces
- Increased capacity for surface agitation



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82

Target Property: Gel Cohesion

More cohesive gels:

- Less likely to adhere to swollen coatings/accretions
- Less likely to leave significant residues
- Generally easier to remove from surfaces

83

Target Property: Increased Moisture Retention

With increased moisture retention:

- Slower delivery
- Possibilities for moisture delivery to sensitive surfaces
- Possibilities for long dwell times

Generally: Increased moisture retention affords greater control by dilating the variable of time

84

Target Property: Thermal Stability

Possible warm/hot and cold applications
- Increasing effectiveness/activity of aqueous preparations
- Manipulating adhesive/coating properties according to T_g

Effect of freezing on gel structure
- Many hydrogels express significant water upon freezing
- Densification of gel network

Effect of heating on gel structure
- Softening of gel structure; loss of gel strength

It could be beneficial to have a gel that could withstand both heating and cooling

85

Target Property: Reduced Possibility for Residues

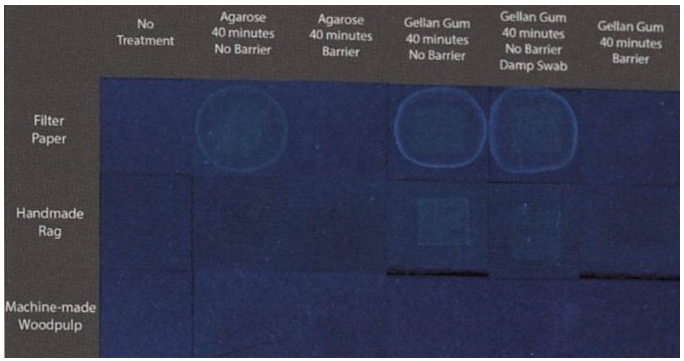
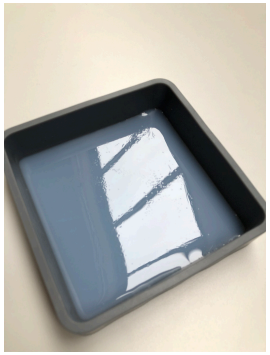
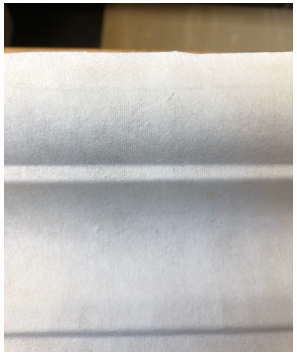


Image adapted from Sullivan, et al., *Gels in the Conservation of Art*, (2017).

40-minute gel exposure tests; UV-induced visible fluorescence

86

Target Property: Optical Clarity


87

NANORESTORE® GELS

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
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88

Nanorestore® Gels: Dry

Nanorestore Gel Dry

- poly(hydroxyethylmethacrylate)/ poly(vinyl pyrrolidone) [pHEMA/PVP] semi-interpenetrated chemical hydrogels (i.e. covalently bonded)
- Available: 'Medium Water Retention' & 'High Water Retention' (MWR & HWR)
- Highly retentive – in some applications, safe for water-sensitive surfaces

Image: CSGI

89

Nanorestore® Gels: Dry

Moisture Retention

Table 1 Compositions (w/w) of the selected semi-IPN hydrogels; HEMA/MBA and HEMA/PVP ratios

	H50	H58	H65
HEMA (%)	25.0	16.8	10.5
MBA (%)	0.2	0.2	0.2
PVP (%)	24.9	25.1	24.4
Water (%)	49.9	57.9	64.9
HEMA/MBA ratio	$1:1 \times 10^{-2}$	$1:1.5 \times 10^{-2}$	$1:2 \times 10^{-2}$
HEMA/PVP ratio	50/50	40/60	30/70

The acronym HXX refers to the XX percentage of water in the reaction mixture

Table 2 Some physicochemical properties of the selected p(HEMA)/PVP, acrylamide [7] and polysaccharide hydrogels

	G (%)	EWC (%)	Water release (mg/cm^2)
H50	90	72	8
H58	78	80	15
H65	74	87	16
Acrylamide "Hard"	95	95	27
Acrylamide "Soft"	88	97	56
AgarArt	-	97	30
Kelcogel	-	97	33

Appl. Phys. A (2014) 114:705–710
DOI 10.1007/s00339-013-8150-0

90

Nanorestore® Gels: Dry

Practical Considerations

- **EUR 18.00/150cm² sheet**
- Very consistent processing
- Clear, somewhat brittle gels
- **Can be loaded with aqueous solutions, microemulsions, structured fluids, some polar solvents**
- **Possible to clean and re-use**

91

Nanorestore® Gels: Dry

Practical Challenges

- MWR and HWR Dry gels can develop cracks and tears
- Gels become unusable if allowed to dry fully
- Gels can support biological growth; cleaning is difficult
- If loaded with solvent, further use for aqueous delivery is not recommended

92

Nanorestore® Gels: Dry Applications

Recommended Applications

- Use on “flat” surfaces
- Humidification, surface cleaning, stain reduction
- Controlled delivery on water-sensitive surfaces
- Slow swelling and dewetting of adhesive residues and coatings
- Cracked/porous surfaces where residues are a concern

93

Nanorestore® Gels: Dry Applications

Images: A. Camp

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94

Nanorestore® Gels: Peggy

Nanorestore Gel Peggy

- poly(vinyl alcohol) and poly(vinyl alcohol)/poly(vinyl pyrrolidone) hydrogels
- Available: Peggy 5 [poly(vinyl alcohol)] and Peggy 6 [PVA/PVP] as sheets, gums (erasers), and pens
- Flexible, elastic
- Conforms to rough surfaces (Peggy 6 more so than Peggy 5)

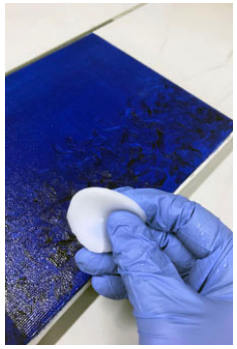


Image: CSGI

95

Nanorestore® Gels: Peggy

Practical Considerations

- **EUR 18.00/150cm^2 sheet**
- Very consistent processing
- Semi-opaque, flexible, elastic gels
- **Can be loaded with aqueous solutions, structured fluids, microemulsions, some polar solvents**
- **Possible to clean and re-use**

96

Nanorestore® Gels: Peggy

Practical Challenges

- Peggy gels less retentive than Dry; Peggy 6 less retentive than Peggy 5
- Gels become unusable if allowed to dry fully
- Peggy gels can support biological growth readily
- More limited solvent compatibility than Dry gels
- If loaded with solvent, further use for aqueous delivery is not recommended

97

Nanorestore® Gels: Peggy

Recommended Applications

- **Use on "flat" or rough surfaces. Peggy 6 conforms better to rough surfaces than Peggy 5**
- **Humidification, surface cleaning, stain reduction**
- **Controlled delivery on sensitive surfaces; limiting mechanical action**
- **Cracked/porous surfaces where residues are a concern**
- **Tape/adhesive removal**
- **Adhesive reactivation**

98

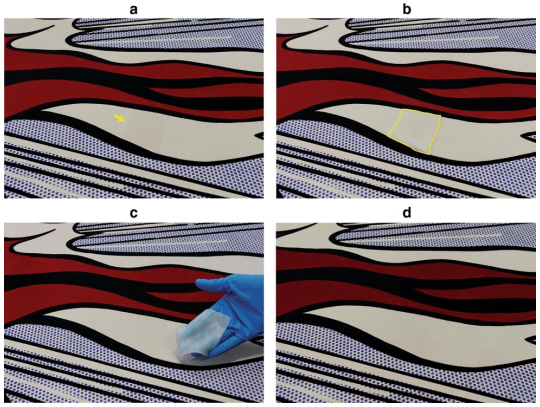
Hydrogel Solvent Compatibility

Because Nanorestore® gels are consistent from batch to batch, their polar solvent compatibility is known:

Gel Dry			Gel Peggy
Benzyl alcohol	2-Propanol	Xylenes	Hydroalcoholic solvents (50%)
Acetic acid	Acetone	Toluene	
Ethylene glycol	Butyl acetate		
2-Methoxyethanol	Cyclohexane		
Ethanolamine	Ethyl acetate		
Propylene glycol	Heptane		
Ethanol	Methyl ethyl ketone		
Methanol	1-Pentanol		
2-Butanol	Propylene Carbonate		

99

Nanorestore® Gels: Peggy



Bartoletti, A., Barker, R., Chelazzi, D. *et al.* Reviving *WHAAM!* a comparative evaluation of cleaning systems for the conservation treatment of Roy Lichtenstein's iconic painting. *Herit Sci* **8,** 9 (2020). https://doi.org/10.1186/s40494-020-0350-2

100

Nanorestore® Gels: Key Decisions

- Surface area to be treated (can be cost prohibitive)
- Improved surface contact (Peggy gels) vs. improved moisture retention (Dry gels)

- *Solvent compatibility*
- *Are other gels feasible?*

101

FLEXIBLE HYDROGELS

102

Formulation Inspiration

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Increasing xanthan gum content could enhance the performance of agar/konjac glucomannan-based system

Dongling Qiao [a], Wenjuan Shi [a], Man Luo [a], Wanting Hu [a], Yuchun Huang [a], Fatang Jiang [a], Fengwei Xie [b,*], Binjia Zhang [c,*]

[a] Glyn O. Phillips Hydrocolloid Research Centre at HBUT, National "111" Center for Cellular Regulation and Molecular Pharmaceutics, School of Food and Biological Engineering, Hubei University of Technology, Wuhan, 430068, China
[b] School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom
[c] Group for Cereals and Oils Processing, College of Food Science and Technology, Huazhong Agricultural University, Wuhan, 430070, China

United States Patent [19]
Musson et al.

[11] **Patent Number: 4,894,250**
[45] **Date of Patent: Jan. 16, 1990**

[54] **THERMO-IRREVERSIBLE EDIBLE GELS OF GLUCOMANNAN AND XANTHAN GUMS**

[75] Inventors: **Gary D. Musson**; **Colin T. Prest**, both of Melton Mowbray, United Kingdom

[73] Assignee: **Mars G.B. Limited**, Berkshire, United Kingdom

[21] Appl. No.: **190,581**

[22] Filed: **May 5, 1988**

[30] **Foreign Application Priority Data**
May 6, 1987 [GB] United Kingdom 8710704

[51] **Int. Cl.**[4] **A23L 1/06**
[52] **U.S. Cl.** **426/573**; 426/575; 426/574
[58] **Field of Search** 426/573, 575, 574

[56] **References Cited**
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2084844	4/1982	United Kingdom .	
2128871	5/1984	United Kingdom .	
2137066	10/1984	United Kingdom .	
2168366	6/1986	United Kingdom .	

Primary Examiner—Jeanette Hunter
Attorney, Agent, or Firm—Curtis, Morris & Safford

[57] **ABSTRACT**

Thermo-irreversible aqueous gels are prepared by subjecting a gellable combination of xanthan gum and a glucomannan gum, preferably from the corms of an Amorphophallus species at a pH above 6 to a heat treatment under conditions of temperature and time to cause the gel to become thermo irreversible. The pH is preferably between 6 and 10 and more especially between 6 and 8. The preferred ratio of xanthan gum to glucomannan is in the range of from 5:95 to 95:5, more especially 1:10 to 10:1 and the preferred concentration of xanthan gum and glucomannan in the aqueous phase is 0.02% to 6%, more preferably 0.5 to 4%, by weight. The thermo irreversible gels of the invention, with the inclusion of food materials, such as minced meat, fruit and vegetables, simulate the texture of natural meat offals and other food structures.

13 Claims, No Drawings

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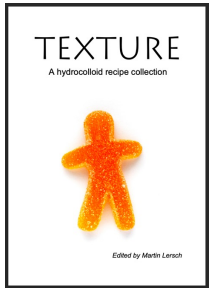
103

Formulation Inspiration



AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
RIGA, LATVIA 1–4 AUGUST 2023

104

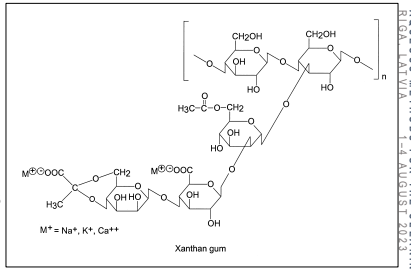
XANTHAN-KONJAC HYDROGELS

105

Xanthan Gum

Bacterial branched ionic gum

- Cellulose backbone
- Anionic trisaccharide side chains



Xanthan gum

Practical Considerations

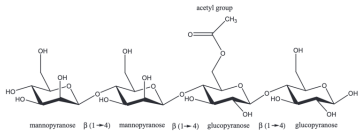
- **Inexpensive (USD 6.80/100g)**
- **Readily hydrates in cold water**
- Typical concentrations: **0.75–1.5%**
- **Very viscous solutions**
- Exceptional **shear thinning**
- **Non-gelling on its own**

106

Konjac Glucomannan

Plant polysaccharide

- Root vegetable
- Glucose/mannose backbone
- Acetyl side groups



Practical Considerations

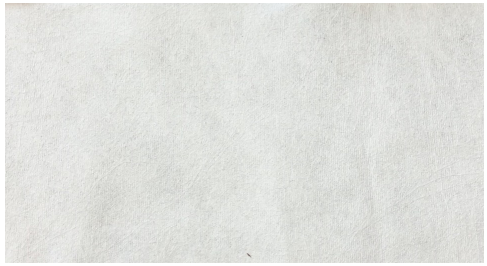
- **Inexpensive (USD 7.00/100g)**
- **Readily hydrates in cold water**
- Typical concentrations: **0.75–1.5%**
- **Very viscous solutions**
- **Shear thinning**
- **Can form a hydrogel by treating with pH 9+ & heating to 90°C**

107

Xanthan/Konjac Hydrogels: Exceptional Elasticity

- **Prepared in the same methods as agar/ose, creating a strong, clear, elastic gel**

1% Xanthan gum
1% Konjac glucomannan



108

Preparing Xanthan/ Konjac Hydrogels

Recommended: immersion circulator

- Set temperature to 190°F
- Prepare a solution of 1% xanthan and a second solution of 1% konjac. Stir to combine*
- Submerge in the water bath for at least one hour
- Carefully remove from bath
- Stir to mix. Pour into Petri dish or other mold. Let cool.
- Rinse to remove unentangled polysaccharide

Microwave method works well, too.

109

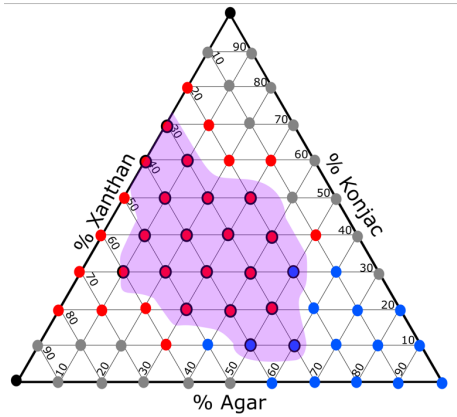
Xanthan/Konjac Hydrogels: Notes

Konjac often has a "fishy" odor depending on its source and purification methods. This odor can be diminished by rinsing or by lowering the pH of the solution.

Xanthan/konjac hydrogels can be pushed to conform to surfaces, and the gel will settle into small surface irregularities

110

Further Modification: Xanthan-Konjac-Agar Hydrogels

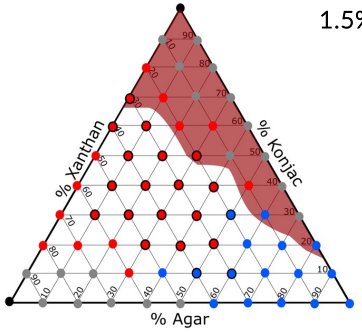


1.5% (w/v) total concentration

- Not a gel - viscous fluid
- Weak gels - poor performance
- Flexible/elastic gel behavior
- Brittle/rigid gel behavior
- Region of interest: "new" gel properties

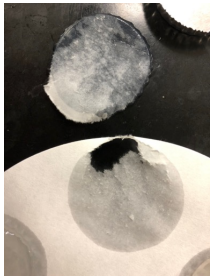
111

Further Modification: Xanthan-Konjac-Agar Hydrogels

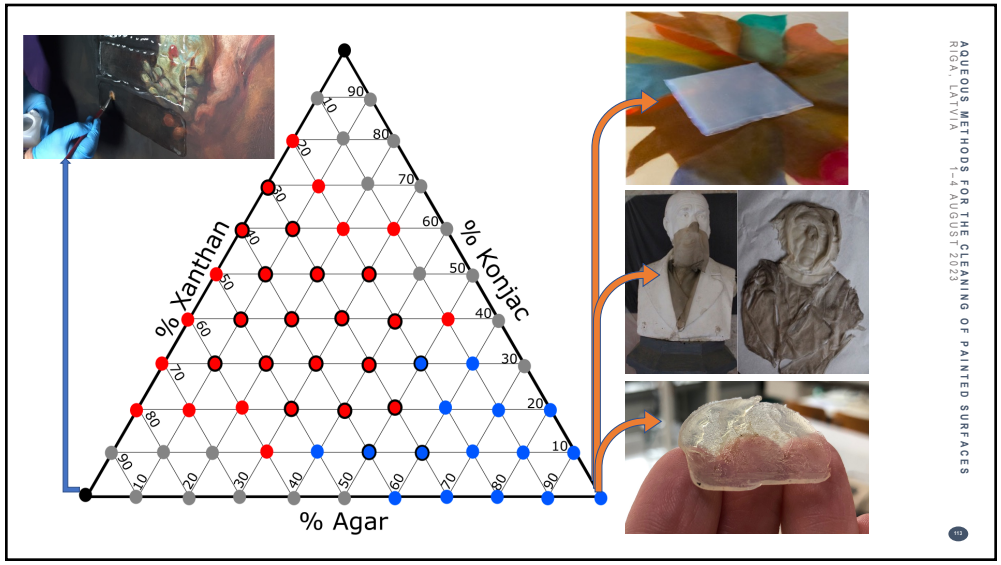


1.5% (w/v) total concentration

- Not a gel - viscous fluid
- Weak gels - poor performance
- Flexible/elastic gel behavior
- Brittle/rigid gel behavior
- Gel adhesion to Whatman filter paper

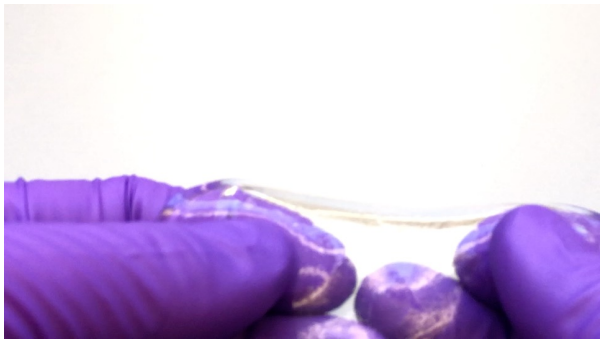


112



113

Further Modification: Xanthan-Konjac-Agar Hydrogels



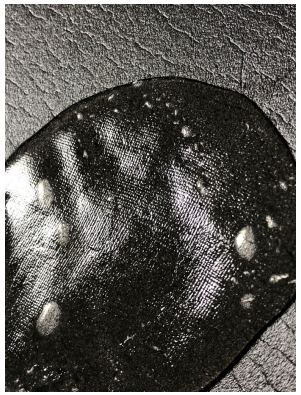
1.5% (w/v) total concentration:
2 parts xanthan
2 parts konjac
1 part agar

- Blend dry ingredients
- SLOW addition to water with mixing
- Heat > 90°C
- Cast

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
RIGA, LATVIA 1-4 AUGUST 2023

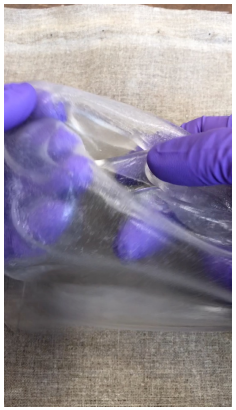
114

Further Modification: Xanthan-Konjac-Agar Hydrogels



115

Further Modification: Xanthan-Konjac-Agar Hydrogels

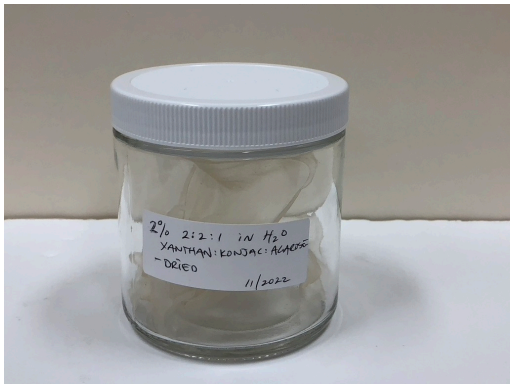


In this video:
2% (w/v) total concentration:
- 2 parts xanthan
- 2 parts konjac
- 1 part agar

Estimated cost, including power for stirring and operation of immersion circulator bath (4 hours):
$0.87 for 20cm x 25cm x 2mm gel

116

Practical Use: Xanthan-Konjac-Agar Hydrogels



"Loading" a cleaning solution:
- Initial preparation of the gel
- Soaking a freshly prepared gel

Xanthan-konjac-agar(ose) gels can be dehydrated and stored.

Dehydrated gels can be rehydrated with aqueous cleaning solutions, with minimal change to gel performance.

117

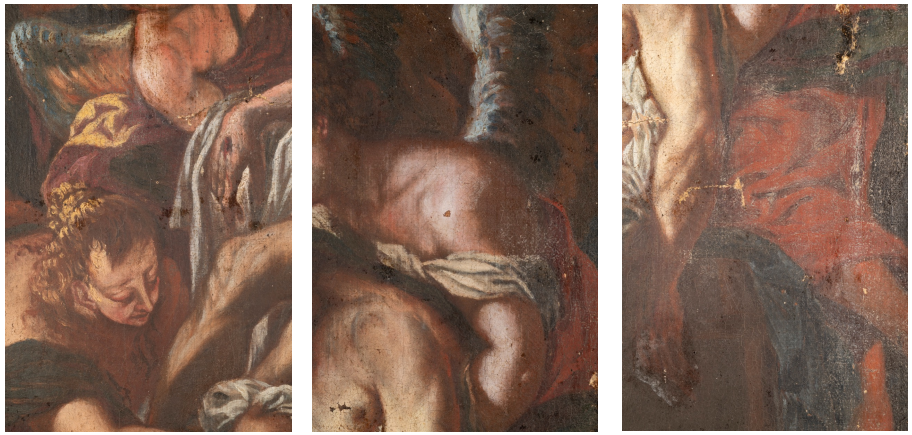
Case Study: GACP1293, Deposition with Angels

- Deaccessioned from Harvard Univ.
- Anecdotes: Used for testing varnishes and cleaning, dating to Gettens and Stout.

- At WUDPAC:
  - Microscopy studies
  - Cleaning experimentation

118

Case Study: Deposition with Angels



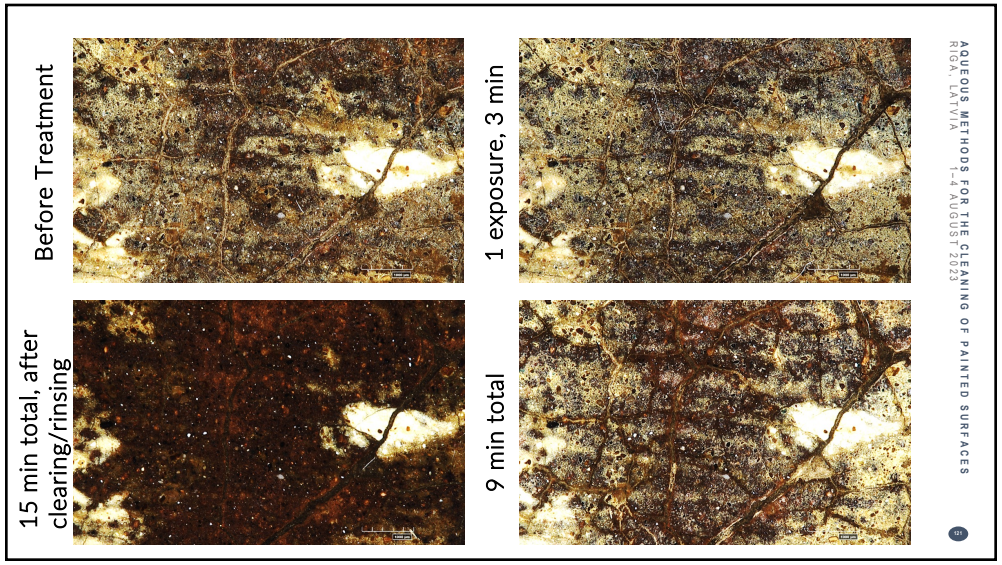
119

Case Study: Deposition with Angels

- Residual varnish: slight effect with alcohols and ketones
- Pigment pickup with other polar solvents
- Aqueous tests:
  - > pH 8: some coating fractions removed
  - Significant improvement with chelating agents; DTPA most effective
  - Additional improvement with deoxycholic acid
- Goal: reduced mechanical action

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
RIGA, LATVIA 1–4 AUGUST 2023

120


Before Treatment
1 exposure, 3 min
15 min total, after clearing/rinsing
9 min total
AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
RIGA, LATVIA 1–4 AUGUST 2023
121

121


Exposure 1
Exposure 2
Clean gel
Exposure 3
Clearance swab
Exposure 4
Exposure 5
Exposure 5 gel surface after cleaning
AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
RIGA, LATVIA 1–4 AUGUST 2023
122

122

Ionic Crosslinking: XKA Gels

Early tests:

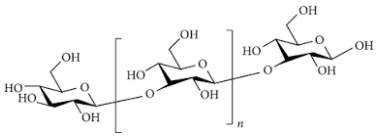
- 0.4g Calcium acetate hydrate/1L solution
- Resulting gels show increased toughness
- Significant reduction of residue autofluorescence on filter paper

123

CURDLAN HYDROGELS

124

Curdlan



Bacterial beta-glucan

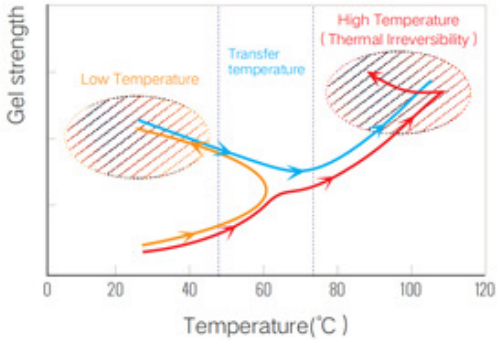
- (1→3)-β-D-glucose polymer, high MW

Practical Considerations

- **Fairly expensive (USD 40.00/100g)**
- Gels upon heating beyond hydration temperature (**heat set**)
- Forms an opaque **elastic, retentive gel** upon heating above 195ºF.
- Thermo-**irreversible; good temperature stability**
- Can form a softer thermo-reversible gel if not heated >150ºF
- **Gel structure, flexibility & toughness depend on solution concentration and solution heating**

125

Preparing Curdlan Hydrogels



Heating below 60C: "soft set" gel, thermoreversible

Heating above 80C: "hard set" gel, thermoirreversible

126

Curdlan Gel Strength: Concentration and Temperature

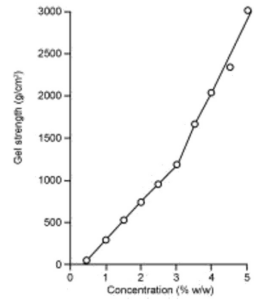


Fig. 20.7 Concentration dependence of gel strength for curdlan at 30 °C[2] (curdlan gel was obtained by heating at 90 °C for 10 min).

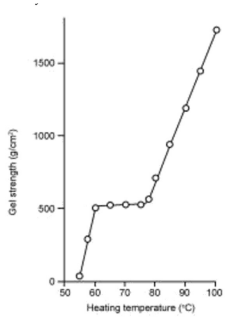


Fig. 20.8 Effect of heating temperature on gel strength of curdlan at a concentration of 3%.[2]

127

127

Preparing Curdlan Hydrogels

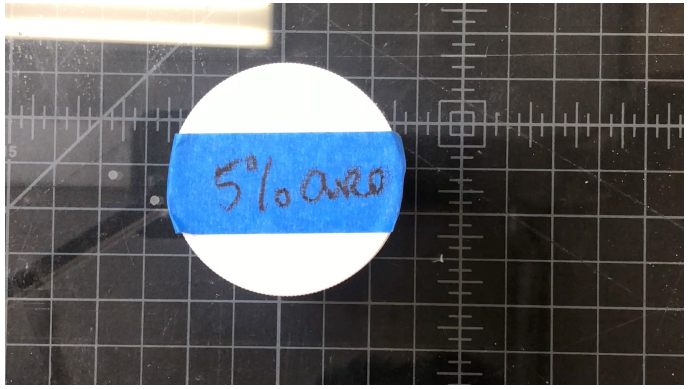
Recommended: immersion circulator

- Set temperature to 195ºF
- Prepare a curdlan slurry, 5-10% (w/v) in distilled water, in a small plastic zip-top baggie. Shake and manipulate to achieve even dispersion.
- Pour a thin layer (~2-3 mm) of the slurry into a flat-bottomed beaker or jar.
- Suspend the container in the water bath for at least 5 minutes, up to 1 hour.
- Allow the curdlan gel to cool. Remove from container.
- Rinse to remove unentangled polysaccharide

128

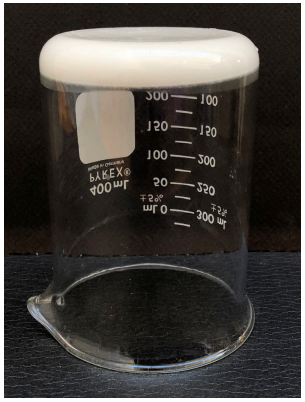
128

Preparing Curdlan Hydrogels



129

Preparing Curdlan Hydrogels



130

Preparing Curdlan Hydrogels

Curdlan gels will take on the shape of any form once the dispersion reaches the heat setting temperature.

Ideas:

- blocks
- sheets
- “noodles”
- lozenges/pointed erasers

131

131

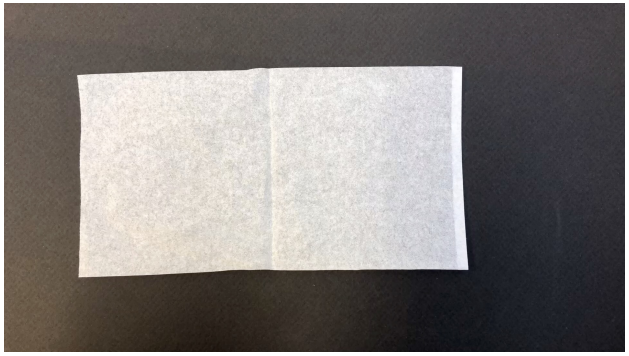
Curdlan Gels: Useful Properties

- Heat setting – additional options for gel preparation
- Subsequent temperature stability
  - Can be warmed/heated
  - Can be frozen!
- Impressive water retention
- Very high gel strength & cohesion

132

132

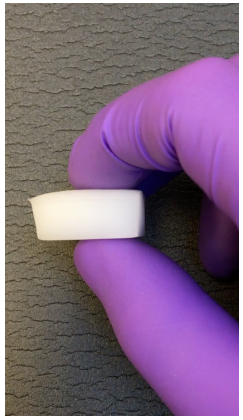
Comparing Curdlan & Peggy Gels

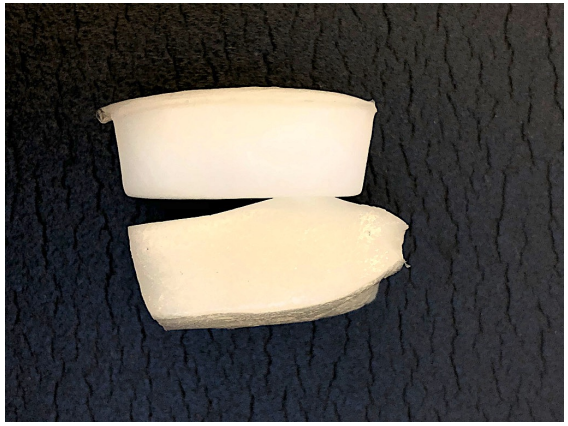


Time-lapse: 30s, water transfer to KimWipe. 10% Curdlan (left) and Peggy 5 Gum (right), both loaded with the same aqueous solution.

133

Comparing Curdlan & Peggy Gels





134

Curdlan Hydrogels: Notes

Curdlan gels will promote biological growth after just a few days; limit air exposure

Curdlan gels can be warmed to increase the activity of diffused moisture

Gel strength decreases with increased inorganic salt concentration and/or solvent in initial formulation; recommended to prepare a gel first and then load it with a cleaning solution

135

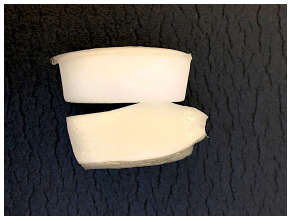
Mechanical Techniques

If the surface can take some amount of agitation:

- **Hydrogels can be loaded with water/solutions and used as a damp sponge or eraser**
- **Hydrogels can be cast or cut to useful shapes**

Consider:

- A cohesive, elastic gel will not leave fragments behind as frequently as a brittle gel
- If the gel is too retentive, the solution may not be delivered as expected



136

Curdlan Hydrogels: Recommended Uses

Controlled humidification:

- *Cast sheets for overall humidification*
- *"Noodles" for humidifying individual creases*

Dampened eraser:

- *Cut/cast blocks*

Delivery of aqueous cleaning preparations

137

QUICK NOTE ABOUT CLEARING/RINSING

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
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138

Clearing Aqueous Solutions

"pH-Adjusted Water"

- **dilute mixtures of acetic acid and ammonium hydroxide**
- **both components volatile**
- **buffered between 3.8-5.6 and 8.3-10.1**
- **ionic strength determined by concentration**
- **formulate according to pH used and estimated conductivity of surface**

139

SUMMARY

140

Selected Gel Characteristics

GEL	COST	Cold water soluble?	Water retentive?	Requires heating?	Solvent stabilizer?	Useful property	Primary use
Cellulose ethers	Inexpensive	Yes	No	No	Minimal	Versatile	Thickener
Pemulen TR-2	Inexpensive	Yes	No	No	Very good	Versatile	Gel/emulsion
Xanthan Gum	Inexpensive	Yes	No	No	Good	Versatile	Gel/emulsion
Agarose	Very Exp.	No	Yes, varies	Yes	Minimal	Syneresis	Hydrogel
Nanorestore Dry	Expensive	No	**Yes, very!**	No	Some polar	Great retention	Hydrogel
Nanorestore Peggy	Expensive	No	Yes, slight	No	Some polar	Elastic & retentive	Hydrogel
Xanthan/Konjac /Agar(ose)	Somewhat Inexpensive	No	Yes, slight	Yes	Minimal	Elastic, self-produced	Hydrogel
Curdlan	Somewhat Expensive	No	Yes, varies	Yes	Some polar	Retentive, self-produced	Hydrogel

141

RESIDUES AND RINSING

142

Residues

- **Increased likelihood of residues:**
  - "Fresh" gels – *rinse with distilled water to remove unentangled polysaccharides*
  - Lower concentration gels
  - Softer gels
  - Cracked, porous surfaces

- **Reduced incidence of residues:**
  - Tissue barrier *but with altered capillary action*
  - Temporary hydrophobization
  - Clear using appropriate rinsing solution* loaded into gel

143

Residues Visualization

- **Qualitative examination:**
  - UV-induced visible luminescence
  - Particularly useful for absorbent surfaces
    - See: Sullivan (2017)
  - Optical microscopy

144

Practical Considerations: Rinsing/Clearing

Questions to consider:

- How porous is the substrate/structure?
- Are there any sensitivities to moisture to anticipate?
- Does the delivery method work well with the structure and condition of the surface?
- How likely is clearance? Are you willing to leave material behind as part of your treatment?

145

Clearing Aqueous Solutions

- **Goal 1: prevent precipitation of solubilized constituents**
- **Goal 2: prevent new solubilization of preserved materials**
- **Sub-goal: continue/slow down cleaning**

146

Clearing Aqueous Solutions

"pH-Adjusted Water"

- **dilute mixtures of acetic acid and ammonium hydroxide**
- **both components volatile**
- **buffered between 3.8-5.6 and 8.3-10.1**
- **ionic strength determined by concentration**
- **formulate according to pH used and estimated conductivity of surface**

147

AFTERNOON SESSION: EXPERIMENTING WITH SPREADABLE GELS & HYDROGELS

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
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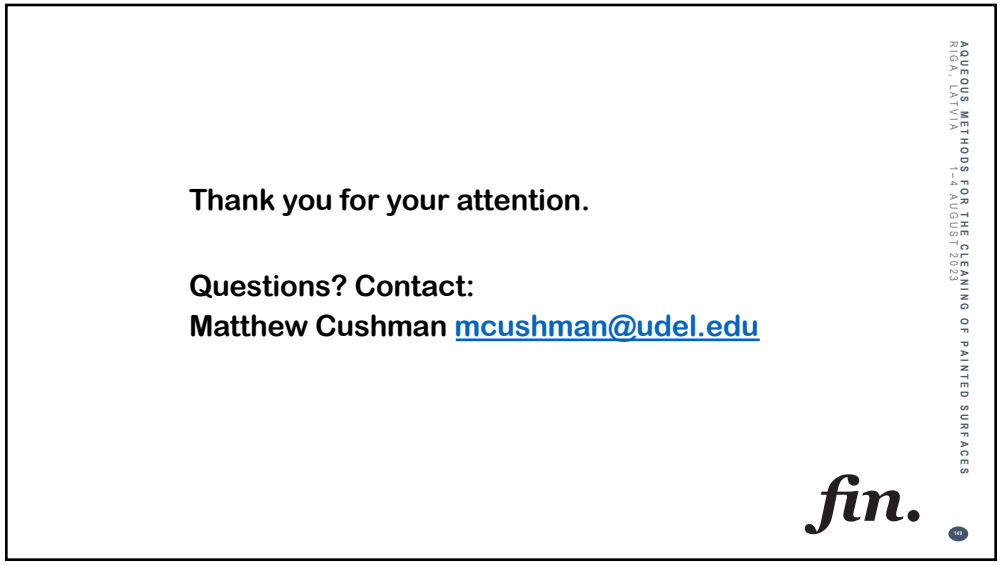
148


Thank you for your attention.
Questions? Contact:
Matthew Cushman mcushman@udel.edu
fin.
AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
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149

149